# Determination of Nitrite, Nitrate, and Bromide in Seawater by UV/Vis Detection after Suppression

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## 1. Introduction

The determination of concentration levels of nitrite, nitrate, and bromide in water environments is important for the control of water quality and for the investigation of pollution of eutrophication.[1] However, as the concentration of the ions in seawater is in general low, sensitive methods must be applied for analysis. In addition, the complex nature of seawater matrix can challenge sensitive determination of traces of nitrite, nitrate, and bromide. Since the anions absorb UV light in the range 200-220 nm in contrast to highly concentrated chloride, they can be measured with high selectivity and sensitivity by ion chromatography and UV detection.

The IC system with electrolytic suppression and UV/Vis detection provides sensitive measurements of anions in complex samples like seawater. In this work, nitrite, nitrate, and bromide were analysed by conductivity and subsequent UV/Vis detection after suppression of the eluent. High linearity, low limits of detection as well as excellent precision of retention time and peak area were achieved.

## 2. Materials and Methods

### 2.1 Analytical Conditions

The analysis of seawater was performed using a Shimadzu HPLC system equipped with a CDD-10A$_{VP}$ conductivity detector and SPD-20A UV detector. Chromatographic separations were carried out using a Shim-pack IC-SA4 (150 L x 4.6 mm ID, 3.5 µm). Analytical conditions are further specified in Table 1.

**Table. 1:** Analytical conditions.

| | |
|---|---|
| LC system | Shimadzu HPLC |
| Column | Shim-pack IC-SA4 (150 L x 4.6 mm ID, 3.5 µm) |
| Mobile phase | 1.7 mmol/L sodium carbonate / 5.0 mmol/L sodium bicarbonate |
| Flow rate | 0.8 mL/min; isocratic elution |
| Column temperature | 50 ºC |
| Injection volume | 50 µL |
| 1st detector | Suppressed conductivity |
| Suppression | Electrolytically regenerated |
| 2nd detector | UV |
| Flow cell | Semi-micro |
| Wavelength | 218 nm |

### 2.2 Sample Preparation

The seawater samples from the North Sea were diluted 1/20 (v/v) by water and filtered through 0.45 µm PET syringe filters.

## 3. Results

### 3.1 Precision of Retention Time and Peak Area and Calibration Curves

Figure 1 shows an overlay of five chromatograms for separation of seven standard anions on Shim-pack IC-SA4 column with suppressed conductivity and UV/Vis detection, respectively. The three anions, nitrate, bromide, and nitrate show UV absorption (**magenta**) in contrast to fluoride, chloride, phosphate, and sulfate ions (**black**).

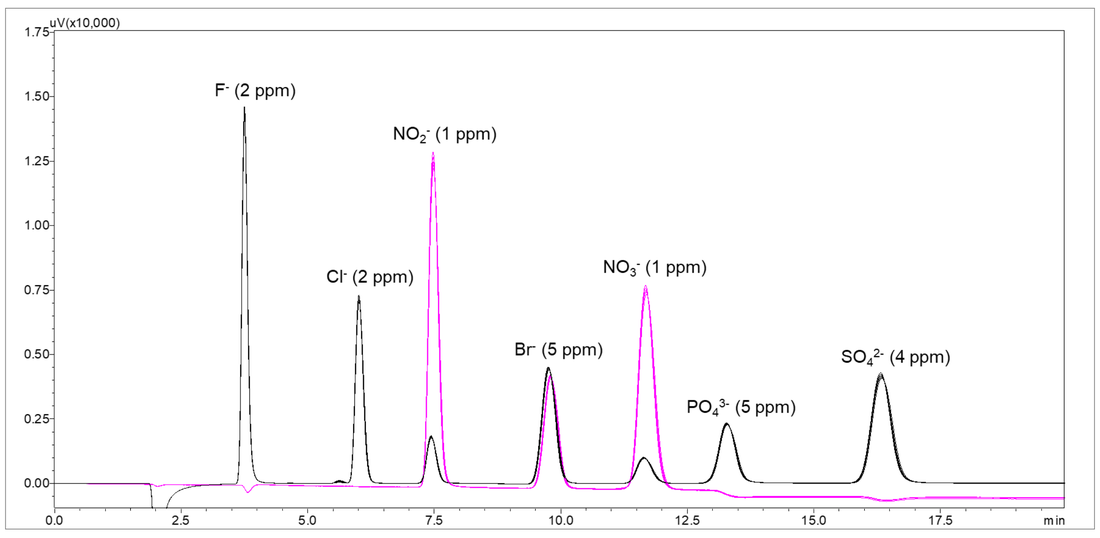


**Figure 1**: Overlay of five chromatograms of standard anions (**black**: conductivity; **magenta**: UV).

As shown in Table 2, all anions are determined within 17.5 min with high precision for retention time (RSD ≤ 0.07 %) and peak area (RSD ≤ 0.51 %) for both detectors.

**Table 2:** Retention time and peak area reproducibility (n=5) for suppressed conductivity (all anions) and UV/Vis detection (nitrate, bromide, and nitrate).

| Anion | $t_R$ precision (RSD [%]) | Area precision (RSD [%]) |
|---|---|---|
| Fluoride | 0.03 | 0.03 |
| Chloride | 0.04 | 0.51 |
| Nitrite | 0.06 / 0.05 | 0.10 / 0.07 |
| Bromide | 0.06 / 0.06 | 0.06 / 0.20 |
| Nitrate | 0.07 / 0.06 | 0.08 / 0.06 |
| Phosphate | 0.04 | 0.21 |
| Sulfate | 0.06 | 0.12 |

**Figure 2** shows linearity in the calibration range of 0.1-5 ppm obtained with external standards (0.1, 0.2, 0.5, 1, 5 ppm) of nitrite, bromide, and nitrate. The coefficient of determination of $R_2$ ≥ 0.9999 for both detectors, as shown in Table 3. Limits of detection (LOD) were determined for 0.1 ppm standards using ASTM method for noise calculation in the range of 15-20 min and detection limit coefficient 3.3. As shown in **Table 3**, the LOD for nitrite and nitrate detected with UV/Vis detection (0.9 ppb and 1.4 ppb, respectively) are lower compared to suppressed conductivity (2.9 ppb and 4.8 ppb, respectively). In contrast to nitrate and nitrate, bromide has lower LOD with suppressed conductivity (5.3 ppb) compared to UV/Vis detection (12.8 ppb).

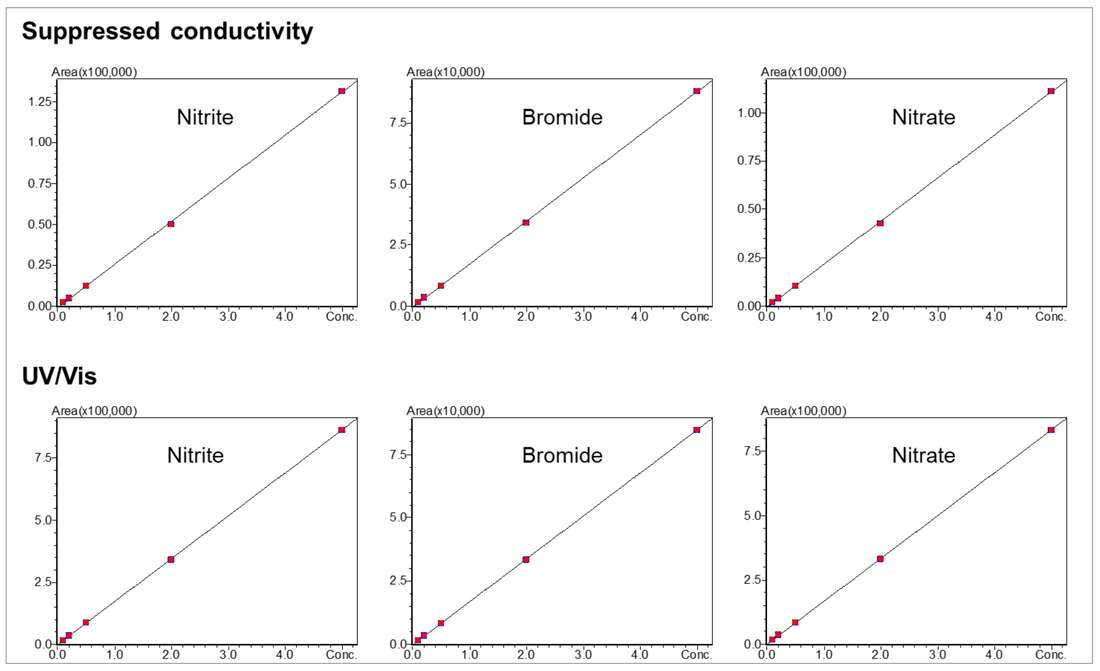


**Figure 2:** Calibration curves for standards of nitrite, bromide, and nitrate obtained with suppressed conductivity (**top**), and UV/Vis detection (**bottom**).

**Table 3:** Calibration range, linearity and LOD for suppressed conductivity and UV detection.

| Anion | Calibration Range [ppm] | Linearity | LOD [ppb] Conductivity / UV |
|---|---|---|---|
| Nitrite | 0.1-5 | ≥ 0.9999 | 2.9 / 0.9 |
| Bromide | 0.1-5 | ≥ 0.9999 | 5.3 / 12.8 |
| Nitrate | 0.1-5 | ≥ 0.9999 | 4.8 / 1.4 |

### 3.2 Analysis of Seawater Samples

**Figure 3** (left) shows separation of anions in diluted seawater (1/20 (v/v by water) using suppressed conductivity and UV/Vis detection. The peak tracking was also supported by spiking the diluted samples with 0.1 ppm nitrite, 2.5 ppm bromide, and 0.1 ppm nitrate as shown in **Figure 3** (right). In the samples, bromide and nitrate were determined. Both anions were detected only with UV/Vis detection, while bromide was detected with suppressed conductivity. In three different seawater samples, the concentration of bromide was determined using external calibration method in the range of 65.1 to 65.9 ppm.

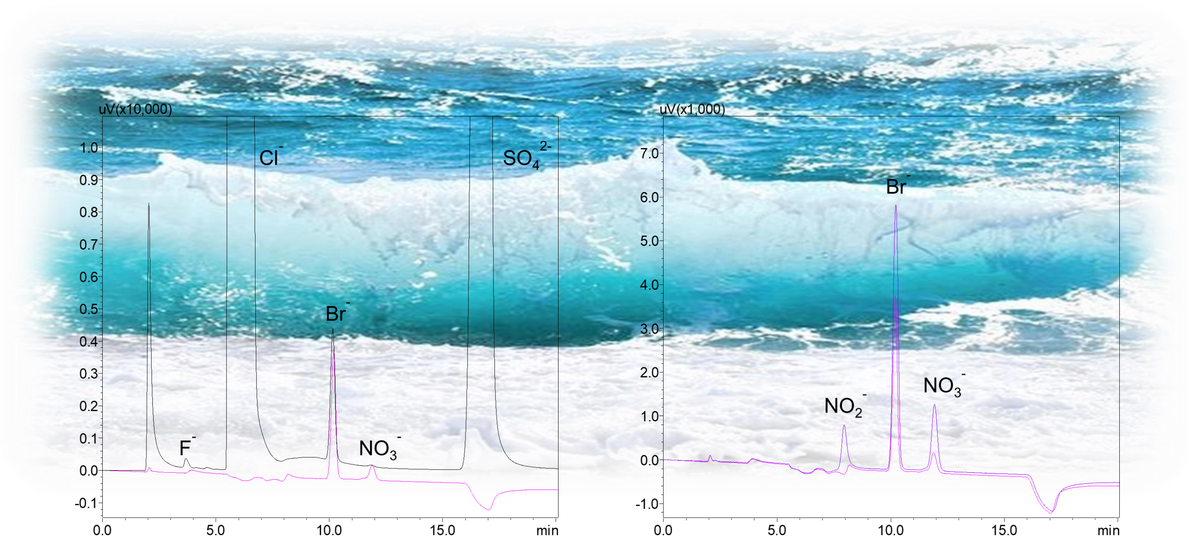


**Figure 3: left**: suppressed conductivity (**black**) and UV/Vis (**magenta**) chromatogram of seawater diluted 1/20 (v/v) with water ; **right**: UV/Vis chromatograms of non-spiked (magenta) and spiked (purpe) seawater with 0.1 ppm nitrite, 2.5 ppm bromide, and 0.1 ppm nitrate.

## 4. Conclusion

The Shimadzu HPLC with electrolytic suppression and UV/Vis detection provides sensitive measurements of anions in complex samples like seawater. Due to the different selectivity and sensitivity, both detectors can be complementary applied for qualitative and quantitative analysis of anions.

### References

[1] Ito, K., et al., *Analytical and bioanalytical chemistry*, *404*(8), 2513-2517.